
Acids and bases

Answers to worked examples

WE 6.1 Conjugate acids and conjugate bases

Pure ethanoic acid ($\text{CH}_3\text{CO}_2\text{H}$) reacts with liquid ammonia (NH_3) to form ions in a proton transfer equilibrium. Write an equation for the reaction and identify the conjugate acid base pairs involved. (Omit state symbols.)

Strategy

Write out the equation for the equilibrium by deciding which reactant is most likely to be the proton donor (acid). The product formed by the loss of a proton is its conjugate base.

Solution



The conjugate acid–base pairs are $\text{CH}_3\text{CO}_2\text{H} / \text{CH}_3\text{CO}_2^-$ and $\text{NH}_4^+ / \text{NH}_3$.

WE 6.3 Calculating the pH of a weak acid

A solution of ethanoic acid in water has a pH of 3.2. Calculate the concentration of the solution.

Strategy

Ethanoic acid is a weak acid and it is not fully ionized in water. This means that the $[\text{H}_3\text{O}^+(\text{aq})]$ concentration that can be calculated using Equation 6.5 from the pH is not the same as the acid concentration. The acid concentration has to be calculated using Equation 6.2 for the acidity constant, K_a . In addition, two assumptions have to be made to complete the calculation; firstly, that the $[\text{H}_3\text{O}^+(\text{aq})] = [\text{A}^-(\text{aq})]$ which ignores the $[\text{H}_3\text{O}^+(\text{aq})]$ generated by the self ionization of water; secondly that the $[\text{HA}(\text{aq})]$ is equal to the concentration of HA at equilibrium.

Solution

Use Equation 6.5 to calculate the $[\text{H}_3\text{O}^+(\text{aq})]$,

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = 3.2$$

$$\text{Therefore } [\text{H}_3\text{O}^+] = 10^{-3.2} = 6.3 \times 10^{-4} \text{ mol dm}^{-3}.$$

Use Equation 6.2 and the assumptions described in the strategy,

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})]^2}{[\text{CH}_3\text{CO}_2\text{H}(\text{aq})]}, \text{ so}$$

$$\begin{aligned} [\text{CH}_3\text{CO}_2\text{H}(\text{aq})] &= \frac{[\text{H}_3\text{O}^+(\text{aq})]^2}{K_a} \\ &= \frac{(6.3 \times 10^{-4} \text{ mol dm}^{-3})^2}{1.7 \times 10^{-5} \text{ mol dm}^{-3}} \\ &= 0.02 \text{ mol dm}^{-3} \end{aligned}$$

WE 6.5 Buffer solutions

Calculate the pH of a buffer solution made by mixing 250 cm³ of 0.250 mol dm⁻³ methanoic acid (HCO₂H) and 500 cm³ of 0.500 mol dm⁻³ sodium methanoate (p*K*_a for methanoic acid is 3.75 at 298 K). *Hint*: In this case the concentrations of acid and conjugate base in the buffer are different from those in the solutions added to make it because they dilute one another when they are mixed. Remember to take this dilution into account.

Strategy

Calculate the new concentrations of acid and conjugate base in the buffer based on the new volume of the solution and then use these concentrations in Equation 6.17 (p.282) to calculate the pH.

Solution

$$\begin{aligned}\text{Total volume} &= 250 \text{ cm}^3 + 500 \text{ cm}^3 \\ &= 750 \text{ cm}^3\end{aligned}$$

Since the molarity is defined as number of moles in 1 dm⁻³ (1000 cm³), number of moles in the aliquots added together can be calculated as follows:

$$\text{The buffer solution contains } \frac{0.250}{4} \text{ mol HCO}_2\text{H and } \frac{0.500}{2} \text{ mol HCO}_2^-.$$

The concentration of these species in the 0.750 dm³ solution is

$$[\text{acid}] = \frac{0.250 \text{ mol}}{4 \times 0.750 \text{ dm}^3} = 0.0833 \text{ mol dm}^3$$

$$[\text{conjugate base}] = \frac{0.500 \text{ mol}}{2 \times 0.750 \text{ dm}^3} = 0.333 \text{ mol dm}^3$$

$$\text{Using Equation 6.17, } \text{pH} = \text{p}K_a + \log_{10} \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\begin{aligned} \text{pH} &= 3.75 + \log_{10} \frac{(0.333)}{(0.0833)} \\ &= 3.75 + \log_{10}(4.00) \\ &= 4.35 \end{aligned}$$

WE 6.7 Lewis acids and bases

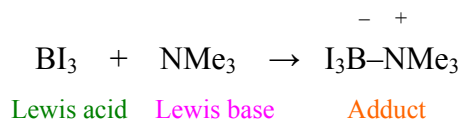
Identify the Lewis acid and the Lewis base in the reaction between boron triiodide, BI₃, and trimethylamine, Me₃N. What is the product of the reaction?

Strategy

The Lewis acid is an electron pair acceptor, therefore the Lewis acid will be electron deficient so that it can interact with the electron pair.

Solution

In this reaction, BI₃ has only 6 valence electrons, so is a Lewis acid, accepting two electrons to fill the octet. NMe₃ has a lone pair on the nitrogen atom, so is a Lewis base.



Answers to boxes

Box 6.1 Solvation

Suggest why sucrose does not dissolve in hexane.

Strategy

Consider the properties which are required from a solvent to solubilise polar molecules such as sucrose.

Solution

Hexane is non-polar, so unable to form strong intermolecular interactions with sucrose. The intermolecular interactions in solid sucrose are stronger than the sucrose-hexane interactions, so sucrose does not dissolve.

Box 6.3 Acidic water in disused mines

What is the concentration of H_3O^+ in a solution of pH -3.6 ?

Strategy

The pH can be directly calculated from Equation 6.5.

Solution

From Equation 6.5

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -3.6$$

$$\log_{10}[\text{H}_3\text{O}^+] = 3.6,$$

$$\begin{aligned} \text{Taking the inverse logarithm of both sides gives } [\text{H}_3\text{O}^+] &= 10^{3.6} \\ &= 4000 \text{ mol dm}^{-3} \end{aligned}$$

Box 6.5 Buffering in the blood

If blood pH rises above 7.45, a potentially life-threatening condition called *alkalosis* can result. This can happen in patients who are hyperventilating from severe anxiety, or in climbers suffering from oxygen deficiency at high altitude. One way to treat alkalosis is to get the patient to breathe into a bag so that the exhaled CO_2 is re-inhaled. Use the above equilibria to explain how this brings down blood pH.

Strategy

Using Le Chatelier's principle and the carbonate equilibria given in Box 6.5, consider what the effect of increasing the carbon dioxide levels has on the amount of $[\text{H}_3\text{O}^+(\text{aq})]$ in the blood.

Solution

$[\text{CO}_2(\text{g})]$ in the lungs increases as the exhaled CO_2 is re-inhaled. This increases $[\text{CO}_2(\text{aq})]$ in the blood. This pushes the positions of equilibrium in the three equilibria to the right hand side. The overall effect is to increase the concentration of $[\text{H}_3\text{O}^+(\text{aq})]$ in the blood, thus lowering the pH.

Box 6.7 Superacids

Use VSEPR theory to predict the shapes of the SbF_5 molecule and the SbF_6^- anion.
Hint: Refer to Chapter 4 for the background to VSEPR theory if you need help.

Strategy

For neutral species, count up the number of electrons around the central atom and determine the number of bond pairs and lone pairs. Place lone pairs strategically to avoid interactions at 90° . For the anions, remember to add on the electrons for the negative charge.

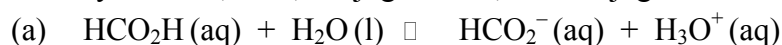
Solution

SbF₅: 5 electrons from Sb and 5 electrons from 5F. 10 electrons around Sb, so 5 electron pairs. Based on a trigonal bipyramidal with no lone pairs. SbF₅ is **trigonal bipyramidal**.

SbF₆⁻: 5 electrons from Sb, 6 electrons from 6F and 1 electron from the negative charge. 12 electrons around Sb, so 6 electron pairs. Based on an octahedron with no lone pairs. SbF₆⁻ is **octahedral**.

Answers to end of chapter questions

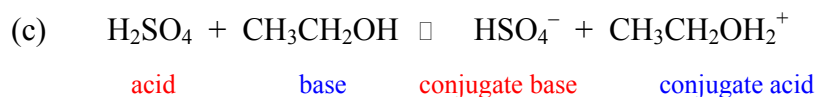
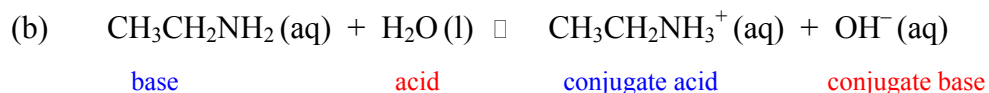
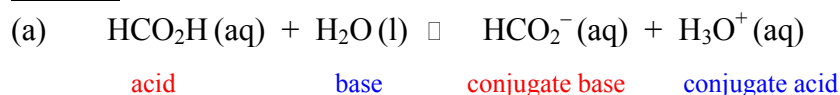
1. Identify the acid, base, conjugate acid, and conjugate base in the following equilibria.



Strategy

Write out the equation for the equilibrium by deciding which reactant is most likely to be the proton donor (acid). The product formed by the loss of a proton is its conjugate base.

Solution



3. K_w for water at 40°C is $3.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$. Is pH 7 neutral, acidic, or basic for an aqueous solution at this temperature?

Strategy

The equation for the self ionization of water is $2 \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$

The $[\text{OH}^-]$ is therefore equal to the $[\text{H}_3\text{O}^+]$ meaning that the $[\text{H}_3\text{O}^+]$ can be calculated from K_w . The $[\text{H}_3\text{O}^+ (\text{aq})]$ concentration can then be used with Equation 6.5 to calculate the pH.

Solution

$$K_w = 3.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} = [\text{H}_3\text{O}^+ (\text{aq})][\text{OH}^- (\text{aq})]$$

For pure water $[\text{H}_3\text{O}^+ (\text{aq})] = [\text{OH}^- (\text{aq})]$,

$$[\text{H}_3\text{O}^+ (\text{aq})] = (3.0 \times 10^{-14})^{1/2} = 1.7 \times 10^{-7} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = 6.8$$

At 40°C, pure water has a pH of 6.8, so this pH corresponds to neutrality. Any pH below this is acidic and any pH above this is basic. This means that pH 7 is basic at 40°C.

5. Hydroxylamine (NH_2OH) is a weak base. A 0.20 mol dm^{-3} solution of hydroxylamine has a pH of 9.7.
- Calculate K_b and $\text{p}K_b$ for hydroxylamine.
 - What is the $\text{p}K_a$ of NH_3OH^+ ?

Strategy

By using Equation 6.8, $\text{pH} + \text{pOH} = 14$, pOH can be calculated by difference. Using the K_b equation (6.5) the $\text{p}K_b$ can be calculated

Solution

(a) $\text{pH} = 9.7$. Using Equation 6.8, $\text{pH} + \text{pOH} = 14.00$.

$$\text{pOH} = 14 - 9.7 = 4.3.$$

$$\text{pOH} = -\log_{10}[\text{OH}^-], \text{ so } [\text{OH}^-] = 10^{-4.3} = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$$

For this reaction



$$K_b = \frac{[\text{NH}_3\text{OH}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{NH}_2\text{OH}(\text{aq})]} = \frac{[\text{OH}^-(\text{aq})]^2}{[\text{NH}_2\text{OH}(\text{aq})]} = \frac{(5.0 \times 10^{-5} \text{ mol dm}^{-3})^2}{0.20 \text{ mol dm}^{-3}}$$

$$= 1.3 \times 10^{-8} \text{ mol dm}^{-3}.$$

$$\text{p}K_b = -\log_{10}(1.3 \times 10^{-8}) = 7.9.$$

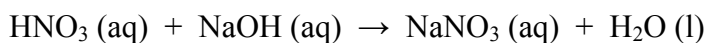
- (b) Using Equation 6.13, $\text{p}K_a + \text{p}K_b = 14.00$ at 298 K
 $\text{p}K_a = 14.0 - 7.9 = 6.1.$

7. In a titration, a solution of $0.200 \text{ mol dm}^{-3}$ NaOH solution is added from a burette to 30.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ HNO₃ solution in a conical flask. Calculate the pH of the solution:
- before any NaOH is added;
 - after addition of 5.0 cm^3 of the NaOH solution;
 - after addition of 10.0 cm^3 of the NaOH solution;
 - at the equivalence point;
 - after addition of 20.0 cm^3 of the NaOH solution.

Strategy

This reaction involves a strong acid reacting with a strong base. All the acid will be fully dissociated and hence the acid concentration will be equal to the H₃O⁺ concentration and pH can be calculated according to Equation 6.5. It is then necessary for the volume of NaOH required to reach the equivalence point to be calculated to answer the questions relating to calculating the pH.

Solution



1 mol HNO₃ (aq) reacts with 1 mol NaOH (aq), so the equivalence point occurs when 15.0 cm^3 of $0.200 \text{ mol dm}^{-3}$ NaOH solution has been added.

- $\text{pH} = -\log_{10}(0.100) = 1.0$
- This is before the equivalence point, so use Equation 6.18 or Equation 6.19.
Using Equation 6.18

$$[\text{H}_3\text{O}^+] = \frac{(0.100 \text{ mol dm}^{-3} \times 0.0300 \text{ dm}^3) - (0.200 \text{ mol dm}^{-3} \times 0.0050 \text{ dm}^3)}{(0.0300 + 0.0050) \text{ dm}^3}$$

$$= 5.7 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}(5.7 \times 10^{-2}) = 1.2$$

(c) This is also before the equivalence point. Using Equation 6.19

$$[\text{H}_3\text{O}^+] = \frac{(0.100 \text{ mol dm}^{-3} \times 0.0300 \text{ dm}^3) - (0.200 \text{ mol dm}^{-3} \times 0.0100 \text{ dm}^3)}{(0.0300 + 0.0100) \text{ dm}^3}$$

$$= 2.5 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}(2.5 \times 10^{-2}) = 1.6$$

(d) Since the titration is between a strong acid and a strong base the equivalence point occurs at pH 7.0.

(e) This is after the equivalence point. The solution contains 5.0 cm³ unreacted NaOH in a total volume of 50.0 cm³.

[OH⁻] is given by

$$[\text{OH}^-(\text{aq})] = \frac{(0.200 \text{ mol dm}^{-3} \times 0.0050 \text{ dm}^3)}{0.05000 \text{ dm}^3} = 0.020 \text{ mol dm}^{-3}$$

$$\text{pOH} = -\log_{10}[\text{OH}^-] = -\log_{10}(0.020) = 1.7$$

Using Equation 6.8, pH + pOH = 14.00 at 298 K,

$$\text{pH} = 14 - \text{pOH} = 14 - 1.7 = 12.3$$

9. Estimate p*K*_{a1}, for the following oxoacids (a) HBrO₃, (b) H₂SeO₃, (c) H₂CO₃. The actual values of p*K*_{a1} and p*K*_{a2} for H₂CO₃ are 6.35 and 10.33, respectively. Suggest a reason for the large difference between these and your calculated values.

Strategy

By using Table 6.5 and the information given on pp.291–2, the values of p*K*_{a1} can be estimated for the oxoacids.

Solution

- (a) For HBrO₃, *n* – *m* = 2, so p*K*_{a1} is likely to be between –3 and 0.8.
 (b) For H₂SeO₃, *n* – *m* = 1, so p*K*_{a1} is likely to be between 1.8 and 3.3.
 (c) For H₂CO₃, *n* – *m* = 1, so p*K*_{a1} is likely to be between 1.8 and 3.3.

The estimated pK_{a1} value suggests that H_2CO_3 is much stronger than it is in reality. The difference arises because much of the H_2CO_3 in aqueous solution is in the form of dissolved CO_2 :

